California Environmental Protection Agency

Air Resources Board

Engineering and Laboratory Branch
Monitoring and Laboratory Division

SOP MLD ES06

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF EXEMPT AND PROHIBITED COMPOUNDS IN CONSUMER PRODUCTS BY HEADSPACE GAS CHROMATOGRAPHY/MASS SPECTROMETRY

March 10, 1998, Revision 1

1 INTRODUCTION

This document describes a method for the analysis of consumer products for those compounds which are identified as "exempt" or prohibited under Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Articles 1 and 2, Sections 94500-94517 and selected compounds that are identified as Toxic Air Contaminants under Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 7, Section 93000. Under the regulations, many compounds, mostly chlorofluorocarbons, have been exempted from the definition of "Volatile Organic Compound (VOC) " due to their low reactivity in the atmosphere. These compounds are not significant in the formation of ozone in the lower atmosphere. However, some of the exempt compounds have been shown to deplete ozone in the upper atmosphere and are prohibited to be used in consumer products manufactured for sale in California on or after January 1, 1993. In addition, Section 94502(e) prohibits the sale of antiperspirants and deodorants containing any compound identified by the Air Resources Board (ARB) as a toxic air contaminant. This method is applicable to liquid consumer products, but may, with modification, be used for solid products as well. With the exception of cyclomethicone (hexamethylcyclotrisiloxane) and dimethicone (hexamethyldisiloxane), the method is not applicable to the class of exempt compounds described as Volatile Methylated Siloxanes (VMS).

2 SUMMARY OF METHOD

This procedure measures volatile exempt and prohibited compounds in consumer products using a headspace gas chromatographic/mass spectrometer (GC/MS) technique. The procedure is an adaptation of Test Methods for Evaluating Solid Waste, USEPA SW-846, Method 8240. Approximately 100 μl of product is introduced into a tared 20 ml headspace vial containing 4.0 ml of 10% water/polyethylene glycol 400 (PEG400) and known amounts of internal standards. The PEG400 dispersant is used to insure that small variations in sample polarity will not affect the analyte(s) partition coefficient. The weight of the product is measured to within 0.1 mg, and the vial is sealed. The vial is equilibrated to 80°C, pressurized to a constant pressure, and an aliquot of the headspace gas is injected into a GC/MS equipped with a 60 m, 0.25 mm id. DB-VRX capillary column. The analytes are separated and quantitated using characteristic ions. After quantitation, the masses of the exempt compounds in the product are calculated, and subtracted from the product VOC as measured by MLD SOP ES01.

3 INTERFERENCES/LIMITATIONS

3.1 Various interferences can be caused by the headspace vial. Each vial must be checked after sealing to prevent leakage. An improperly sealed vial is indicated by low recovery of the internal standards. The vial should never be heated to a temperature exceeding the boiling point of the dispersant (approximately 100°C). Method blanks must be analyzed to insure freedom from contamination by the sampling system.

3.2 Cross contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever a high-level sample is analyzed, it must be followed by a method blank to insure that contamination has not occurred.

4 APPARATUS AND MATERIALS

4.1 Microsyringes, 25, 50, and 100 μl.

4.2 Volumetric flasks, 10, 25. and 50 ml

4.3 Pipettor, capable of delivering 4.0 ml PEG400.

4.4 Balance, capable of accurately weighing to 0.1 mg.

4.5 Vials, 20 ml with crimp-top septa

4.6 Hand crimper for (4.5)

4.7 Positive displacement pipettor, 100 μl

4.8 Headspace Sampling System equivalent to Hewlett-Packard Model 7694

4.9 Gas Chromatograph/Mass Spectrometer System equivalent to Hewlett Packard Models 5890/5971 equipped with a 60m x 0.25mm id, 1.4 μ film, DB-VRX capillary column.

5 REAGENTS

5.1 Stock Solutions: Where possible, standard solutions should be purchased as certified standards. If it is necessary to prepare standard solutions from pure materials, it is recommended that the following steps be taken.

Place approximately 20 ml of methanol in a 25 ml volumetric flask. Allow the flask to stand for approximately 10 minutes, or until all wetted surfaces are dry. Weigh to the nearest 0.1 mg. Using a 100 μl syringe, add pure standard chemical to the methanol. Reweigh and record weight. For gases, it is necessary to add the chemical using a 5 ml valved gas-tight syringe. Dispense the gas slowly just above the methanol, allowing the gas to dissolve in the liquid.

NOTE: Standard solutions of all bromo/chloro/fluorocarbons used in this method can be obtained from AccuStandard Inc., New Haven, CT.

5.2 Internal Standards: Internal standards used in this method are bromochloromethane and 2-bromo-1-chloropropane at concentrations of 20 mg/ml in methanol. All samples, blanks, and calibration standards are spiked with 25 μl of this standard. The surrogate spike standard used is pentafluorobenzene at a concentration of 2.0 mg/ml. All samples, blanks and calibration standards are spiked with 100 μl of the surrogate.

5.3 Control Sample: The Control Sample used for this analysis contains 2-chloro-1,1,1,2-tetrafluoroethane (R-124), dichloromethane, 1,1,1-trichloroethane, and perchloroethylene at concentrations of 1.0 mg/ml.

5.4 4-Bromofluorobenzene Standard: Prepare a standard containing 50 mg/ml of bromofluorobenzene (BFB) in methanol.

5.5 Methanol, pesticide grade or better.

5.6 Dispersant: Add 50 ml reagent grade water to 450 ml of polyethylene glycol 400. Mix well.

6 PROCEDURE

6.1 Tune the mass spectrometer to meet USEPA criteria for bromofluorobenzene (see EPA Method 8240, Table 3, page 12). Record and file the tune parameters. Recommended analysis conditions are:

Mass Range:	45 - 250 amu
Scan time:	approximately 4 sec/scan
Column Temp.:	200° C
Split Ratio:	40/1

Inject 2 μl of BFB standard directly, acquire the spectrum, and generate Pass/Fail report.

6.2 Set up the Headspace Analyzer for the following conditions:

Vial Oven Temperature:	80° C
Loop Temperature:	120° C
Transfer Line Temperature:	120° C
Loop Size:	1 ml
Transfer Gas Flow:	>30 ml/min
Vial Pressure:	15 psi

6.3 Set up the GC/MS system for the following conditions:

MS Tune parameters:	BFB.U
Mass Range:	45-250 amu
Initial Column Temperature:	35° C
Initial Hold Time:	5 min.
Column Program Rate:	10° C/min
Final Column Temperature:	195° C
Injector Temperature:	250° C
MS Interface Temperature:	280° C
Helium Carrier Gas Pressure:	17 psi @ 50° C
	(linear velocity: 26 cm/sec)
Split Ratio:	40/1 (split flow > than transfer flow)

6.4 Calibration Sample: To a clean 20 ml vial, add 4.0 ml of dispersant. Add 100 μl of calibration standard containing 2.0 mg/ml of those compounds listed in Table 1. Add 25 μl of the Internal Standard and 100μl of the surrogate standard. Cap vial with septum and closure. Crimp closure and check for seal tightness (this can be done by twisting the cap). Place the vial into the headspace sampler and analyze. Record the system response for each of the characteristic ions (Table 1) and the calculated relative response factors. Compare the relative response factors for each compound with the historical record. These factors should not vary more than ± 20%. Calibration Samples must be analyzed at least daily.

6.5 Blank: To a clean 20 ml vial, add 4.0 ml of dispersant. Add 25 μl of the Internal Standard and 100 μl of the surrogate standard. Seal cap. Analyze and check to insure that there are no inferences present in the system. Blank analysis must be performed every tenth sample.

6.6 Control Sample: To a clean 20 ml vial, add 4.0 ml of dispersant and 100 μl of Control Standard. Add 25 μl of the Internal Standard and 100 μl of the surrogate standard. Seal and analyze. The results of the Control Sample analysis must fall within the Upper and Lower Warning Limits (UWL, LWL) of the Method Control Chart before analyses may continue. If the results fall outside the UWL or LWL, the Control Sample must be re-analyzed. If the second analysis falls outside the Warnings Limits, or if any Control Sample falls outside the Upper and Lower Control Limits, the analysis must be stopped, the problem investigated and solved, and the system recalibrated. Control Samples must be analyzed every tenth sample.

6.7 Sample Analysis: Using gloves to prevent weighing errors, add 4.0 ml of dispersant to a clean 20 ml vial. Add 25 μl of Internal Standard and 100 μl of the surrogate standard. Place the septum and cap on the vial and weigh to the nearest 0.1 mg. Remove cap and septum, and, using a clean 100 μl displacement pipettor, transfer approximately 100 mg of

sample to the vial. Replace septum and cap and seal the vial. Weigh the vial to the nearest 0.1 mg and record the weight of the sample. Mix the vial contents well. Analyze and record results. Any sample containing ≥0.1 mg of exempt or prohibited VOC must be analyzed in duplicate.

7 DATA INTERPRETATION

7.1 Peak Identification: The identification of an analyte in the sample analyzed must be done by comparing the mass spectrum of the analyte with that of the compound obtained during the calibration analysis. All ions present in the calibration standard mass spectrum with relative intensities of greater than 10% must be in the sample analyte mass spectrum. Relative intensities of the ions present must be within ± 20% of those of the standard mass spectrum (for example, an ion with a relative abundance of 50% in the standard mass spectrum must have a relative abundance between 30 and 70% in the sample analyte). In addition, the relative retention time (RRT, the retention time of the analyte relative to that of the Internal Standard) of the sample analyte must fall within ± 0.01 RRT units of that of the standard.

7.2 Peak Quantitation: After identification, the peak is quantitated using the integratedabundance of the analyte primary ion (see Table 1). Quantitation will take place using the internal standard technique. The mass of the analyte present in the sample is calculated as:

$$\text{mg analyte in sample} = RF \times \frac{(A_s)(C_i)}{(A_i)}$$

Where:

A_s	=	area of characteristic ion of the analyte
A_i	=	area of characteristic ion of the internal standard
C_i	=	mass, in mg, of the respective internal standard
RF	=	Response Factor = $(A_{ic})(C_{st})/(A_{sc})(C_{ic})$ calculated from calibration run, where
A_{ic}	=	area of characteristic ion of the internal standard in calibration
A_{sc}	=	area of characteristic ion of the analyte in the calibration
C_{st}	=	mass, in mg, of the analyte in the calibration
C_{ic}	=	mass, in mg, of the internal standard in the calibration

The percent weight of the exempt compound in the product is calculated as follows:

$$\% \text{ Exempt VOC} = \frac{\text{mg analyte in sample}}{\text{mass of sample, mg}} \times 100$$

8 QUALITY CONTROL

8.1 Prior to use, the GC/MS system must be tuned to meet BFB criteria as described in Section 6.1.

8.2 The GC/MS system must be calibrated daily when in use (Section 6.4) and then a blank and control sample analysis must be made for every ten samples analyzed. Blank analyses must be made when a sample results in the discovery of a sample containing more than 10% of an exempt or prohibited compound. This is to detect possible carry-over into the next analysis.

8.3 Any sample found to have 0.1% or more of a target analyte must be analyzed in duplicate.

8.4 The relative response factor (RF) for each analyte must be recorded after each calibration. The RF must be within ± 20% of the historical average.

8.5 Since the procedure need only analyze for target compounds to a concentration of 0.1% (0.1 mg/100 mg sample), detection limits are to be calculated using seven analyses of analytes at 0.02 mg to verify method sensitivity.

8.6 Instrument linearity need only be verified in the range of 0.1 mg to 10 mg, since it is unlikely that exempt or prohibited compounds will exceed this range. If a sample result exceeds this range, then it shall be reanalyzed using a smaller sample amount.

Table 1
EXEMPT VOC RETENTION TIMES, CHARACTERISTIC ION, AND PRECISION

	RETENTION	PRIMARY	LOD	
RSD COMPOUND	TIME, MIN	ION	UG*	%**
Trifluoromethane	4.14	69	10	9.3
Pentafluoroethane	4.22	51	16	15.1
1,1,1-Trifluoroethane	4.28	69	14	14.1
Chloropentafluoroethane	4.28	85	10	12.6
Bromotrifluoromethane	4.37	69	5	5.2
1,1,1,2-Tetrafluoroethane	4.37	83	3	3.0
1,1,2,2-Tetrafluoromethane	4.44	51	9	6.8
1,1-Difluoroethane	4.54	51	5	4.4
Chlorodifluoromethane	4.62	51	4	4.4
Dichlorodifluoromethane	4.80	85	6	5.6
2-Chloro-1,1,1,2-tetrafluoroethane	4.91	67	12	9.2
1-Chloro-1,1-difluoroethane	5.15	65	2	1.4
1,2-Dichlorodifluoromethane	5.33	85	4	3.6
Bromochlorodifluoromehtane	5.89	85	14	10.5
Dichlorofluoromethane	7.00	67	6	4.4
2,2-Dichloro-1,1,1-trifluoroethane	7.76	83	5	3.4
Trichlorofluoromethane	8.09	101	3	2.4
1,1-Dichloro-1-fluoroethane	8.44	81	8	5.4
Dichloromethane	9.46	84	3	2.3
1,1,2-Trichlorotrifluoroethane	9.58	101	4	3.6
1,2-Dibromotetrafluoroethane	9.74	181	5	3.3
Chloroform	12.45	83	7	6.1
1,1,1-Trichloroethane	13.82	97	4	3.0
Carbon tetrachloride	14.41	117	9	6.7
Hexamethyldisiloxane	14.60	147	10	8.0
Trichloroethylene	15.51	130	3	2.2
Hexamethylcyclotrisiloxane	18.53	207	4	4.6
Perchloroethylene	19.05	164	4	3.0
p-Chlorobenzotrifluoride	20.03	180	4	4.0

* Note 1. Limit of Detection in micrograms component (40 CFR 136, Appendix B).
** Note 2. Percent Relative Standard Deviation, n = 6, 40 micrograms per component.

Appendix A

OPERATION OF HEADSPACE GC/MS

NOTE

The instrument is kept in a "standby" mode - lowering the He flow and increasing the oven temperature. The instrument uses a large amount of He, so at the end of the run, turn EPP C off (set to 0 psi - this is for the headspace pressurization), EPP B is set to 6 - 8 psi, and the split/splitless ratio is turned off (clockwise).

Check the He tank to make sure the pressure is sufficient to last until the next operation (especially over the weekend).

Changing the helium tank must be done quickly. The instrument will shut itself down if the pressure drops too low. If the instrument does shut down, turn off the power (rocker switch, right side of instrument, bottom, rear) then turn it back on. Set the appropriate "EPP B" and "EPPC" flow. Resume operation.

Check the

1. On starting use of the MS - reset the flows to the appropriate value:

   EPP B: 17.0 psi, Enter (press gold key, "Inj. B temp.", screen should read "EPP B")

   EPP C: 15.0 psi, Enter (press gold key, "A", screen should read "EPP C")

2. At this point everything will be controlled by the HP Chem software.

   In the Program Manager - click on "MS Top #1":
   click on "Methods"
   click on "Load"
   click on "Hdsp.m"
   click on "OK"

3. Next have the instrument do an autotune on the MS.
   click on "Tune MS".
   click on "Target tune".
   click on "Tune".
   click on "BFB Tune"

The instrument will automatically optimize and adjust on the peaks 69/219/502 amu. When completed, the screen will give "Tune Complete". It is printer out and kept in the file folder near the MS.

4. The HDSP method being used here is for analysis of exempts and prohibited compounds. A calibration file of 32 compounds (refrigerants and VOC's) has been created in the method for quantitating any of the compounds using the internal standard method. (See Table 1 for a list of the compounds).

5. Preparation of the samples:

   a) Prepare:

      Blank (with I. S.):
      4 ml 10% water/PEG 400
      25 ul Internal Standard mix
      100 ul pentafluorobenzene

      Calibration mix:

      4 ml 10% water/PEG 400
      25 ul Internal Standard
      100 ul pentafluorobenzene surrogate
      100 ul Custom refrigerant mix
      50 ul of VOC mix.

      Check mix:

      4 ml 10% water/PEG 400
      25 ul Internal Standard
      100 ul pentafluorobenzene surrogate
      50 ul VOC mix

      Samples:

      4 ml 10% water/PEG 400
      25 ul Internal Standard
      100 ul pentafluorobenzene surrogate
      100 ul sample

      Internal Standard: 25 ul of approx. 20 mg/ml solution (for 500ug)
      Surrogate: 100 ul of approx. 2 mg/ml solution of pentafluorobenzene (for 200 mg)

6. Headspace sampler: Place all of the headspace vials in numerical sequence in the tray of the headspace autosampler. Use "Tray Advance" and , .

   Press "vial parameters" -
   Press - reads "First Vial 1" (enter or change to "1" if necessary and hit "Enter")
   - reads "Shake [0,1,2] [low]
   - reads "Last Vial #" (enter the total number of vials and hit "Enter")

   All of the rest of the parameters stay as programmed and do not need to be altered. There is a 40 minute cycle time: 20 minutes for the sample to be heated in the oven (80 C) and 20 minutes delay for the GC analysis. The autosampler may be started now.

7. Exit "Tune" (click on "-" for MSD Target Tune - BFB) Click on "close", "Be sure changes are saved. Exit now?" click on "yes"

8. In "Methods" - Hdsp.m program should already be loaded. To check, click on "Load" and see that "hdsp" is highlighted. Click on "OK". The calibration list is in the Hdsp method. No changes should have to be made to the method.

9. Click on "Sequence":
   click on "Load"
   click on "OK"
   click on "Hdsp.s" (this is the sequence file for the Hdsp.m)
   click on "Sequence" again
   click on "edit sample log table"
   line 1 - the keyword, seedname "XXXYY01" is the date (month, day) followed by "01" the beginning designation of the data file. All the data for the sequence being run will be in that month, day and numerical designation. In "Keyword string", enter the date followed by "01".

   When the sequence is initiated the instrument will increment each new sample added to the file.

   line 2 - always the blank + I. S.: (designated as "Blank") enter method as "hdsp"

   line 3 - calibration - make certain of the following:

level	Upd RF	Upd RT	Upd QI
1	replace	replace	replace

   line 4 to end - list the samples, their respective designation, the method and for sample name enter the lab. number in "Sample name.". Any excess lines can be removed by clicking on "Cut", click on "OK".

clink on "Sequence"
click on "Save", will respond with "Save Sequence" "Hdsp.s"
click on "OK"

click on "Method"
click on "Print Brief Format"

click on "Sequence"
click on "load and run sequence"
Screen displays "Start Hdsp.s"
Data file directory: D:\TEH\Data\ If this is not present, enter it.
click on "Run sequence"
All the data will go onto drive D
This initializes and begins the data run.

10. If not done earlier, turn on the headspace sampler: press "Start". This begins the cycle. The first vial will be placed in the oven for 20 minutes. The GC will start on its own from here, when the 20 minutes is complete.

11. If the instrument "locks up" after the first run (no response from the mouse), turn the power off for the data system, then turn it back on.
    load "Method"
    load "Sequence"
    edit "Sequence"
    change the seed name to XXXYY02
    save the "Sequence"
    click on "position and run"
    click on the "calibration" run
    click on "run sequence"
    "Process key words before starting sequence? click on "yes"

DATA ANALYSIS

1. First, load the headspace program:
    click on "Method".
    click on "Load"
    select "hdsp.m" click on "OK".

2. After completion of the sequence, use "Data Analysis" to look at individual data files and print out chromatograms if desired.

    click on "Data Analysis"
    click on "Main Panel"

click of "File"
click on "Load"
scroll down to file [-d-] and select it and click on "OK"
scroll down to file of interest select it and click on "OK"
Chromatogram should appear.

3. To print the chromatogram:

   click on "File"
   clink on "Print"
   be sure "selected window" is chosen and click on "OK"
   enter or change window number then click on "OK"

4. To expand a chromatogram:

   click and hold at the bottom-left corner of the desired area. Move the cursor right to the end of the desired chromatogram. Then move the cursor vertically so that the box created on the screen encloses the desired area. Release the button and the expanded chromatogram should appear.

5. To observe the spectrum of a peak:

   a) Center the arrow and vertical line on the center of the peak and double click right.

   b) To average the spectrum of a peak set the arrow at the bottom-left hand corner of the desired area. Click right and hold. Move the cursor right then up to enclose the desired area. Release the botton. The spectrum of the averaged area should appear.

6. To obtain the difference spectrum, click on the "difference" box in the lower left hand corner.

7. To determine possible matches from the library double click right anywhere in the spectrum of the unknown compound. "Searching" should appear in the bottom-left hand corner of the screen. "PBM Search Results C:\DATABASE\NBS 75K.I." should appear with possible matches. Qual" indicates degree of match, with 100 being perfect. To print the spectrum of the possible match, click on "Print". To get a list of all the possible matches, click on "Statistics", then click on "Print". To exit click on "Done".

SOP Revision History

1. March 10, 1998. Adjusted document font to Times New Roman 12. Inserted appendix B formerly a stand-alone document. Revision History